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Raman and Fourier Transform Infrared Spectroscopy of $CuO-PbO-SiO_2$ Glasses

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ABSTRACT

The structures of glasses in the $CuO-PbO-SiO_2$ system have been investigated by Raman and Fourier Transform Infrared (FTIR) spectroscopy. Glasses of compositions represented by $2xCuO.(1-x)PbO.(1-x)SiO_2$ (x=0 - 0.1) and $3xCuO.(1-x)PbO.2(1-x)SiO_2$ (x=0-0.1) may contain up to 2 and 4 mole % CuO, respectively, without significant changes to the silicate network of the copper-free glasses. The incorporation of 10 mole % CuO in these glasses alters the Raman and FTIR spectra of the copper-free glasses significantly. The observed changes were attributed to a depolymerization of metasilicate and higher polymerized silicate groupings through the creation of non-bridging $Si-O^-$ groups in the silicate network.

I. Introduction

It has been well established that ceramic foodware glazed with lead based frits containing colouring metal ions can release into the food harmful levels of lead but the mechanism by which this occurs has not been extensively studied. Also the extent to which particular metal ions affect the lead release has not been unambiguously determined.

Copper (II) oxide has been found to increase the lead release (1-3), but cobalt (II) oxide has been reported to increase the lead release (4), decrease the lead release (5), or have no effect (3,6) in acid leaching of lead based glazes. The addition of chromium (III) oxide to lead based glazes was found to increase lead release but the extent of this effect varied according to various investigators (3,5). On the other hand it has been reported that the addition of chromium (III) oxide and certain chromate salts can lower the lead release of lead based glazes containing copper in acid leaching tests (7).

Studies that have addressed the structural basis of this phenomenon have been relatively few. A. Krajewski, C.B. Azzoni and coworkers investigated the relationship between chemical durability of lead-based ceramic glazes containing copper and chromium, and the co-ordination of the colouring metal ions as deduced from EPR measurements (9,10). These authors reported a significant correlation between lead release and the percentage of Cu^{2+} ions in sites with C_{2h} or lower symmetry.

Vibrational spectroscopic studies on inorganic glasses containing copper oxide are lacking. As part of an extensive investigation into the structural basis for the dependence of lead release on the presence of colouring transition metal ions, we have carried out a study of the structural changes that occur in the $PbO-SiO_2$ system upon the introduction of CuO. The structural changes were interpreted on the basis of Raman and FTIR (Fourier Transform Infrared Reflectance) spectra.

II. Experimental

Glass samples were prepared by thoroughly mixing reagent grade PbO (Fisher), SiO_2 (Fisher), and CuO (BDH Chemicals). For each composition 50g of the ball milled and dried powders was melted in Pt - 30% Rh crucibles in an electric furnace at temperatures between 900-1200^{o}C for 1-1/2 to 2 hours. The melts were occasionally stirred. The series of glasses prepared are listed in Table 1. The notation used in Table 1 and throughout this paper implies that the mole percentage of CuO in a glass is given by 100x.

Samples for FTIR spectroscopy were prepared by pouring the glass melt into moulds to form discs, approximately 25 mm in diameter and 0.8 mm thick. The discs were not annealed. The central areas of the upper faces were sufficiently smooth and flat to give good reflectance spectra without polishing. Rods, approximately 1 mm in diameter for Raman spectroscopic measurements were pulled directly from the melt.

FTIR spectra were measured on a Nicolet 170 SX Fourier Transform spectrometer using an External Specular Reflectance Attachment from Harrick Scientific Corporation. The infrared beam is reflected off the sample surface at an angle of incidence of 30^{o}, and the energy reflected at the same angle is ratioed against that reflected by a front-surface aluminum mirror.

Raman spectra of the glasses were measured at 90^{o} with respect to excitation with a Spex Ramalog consisting of a 1 metre double-grating (holographic) spectrometer, f/1.4 signal collector, a Lasermate for filtering the Spectraphysics Model 164 Ar^{+} laser lines, an RCA GaAs photo-multiplier with photon counting electronics, and an interfaced computer, Datamate. The laser power was varied from 20 to 200 mW as required. The spectra were measured in the Stokes region of the green laser line (514.5 nm), scanning was carried out in 1 cm^{-1} increments with a 1 s integration time. Multiple scanning was employed to increase the signal-to-noise ratio when required. The recorded spectra were smoothed with a built-in smoothing routine.

III. RESULTS AND DISCUSSION

(1) $2XCuO.(1-x)PbO.(1-x)SiO_2$ Glasses

The base glasses for this study, $PbO.SiO_2$ and $PbO.2SiO_2$, were chosen because their components are major ingredients in lead based ceramic glazes and because the structures of these glasses and their crystalline polymorphs have been characterized by Raman and infrared spectroscopy by other workers (11-16).

$PbO.SiO_2$ can exist as a glass or as one of three crystalline polymorphs commonly denoted as low (L-)$PbSiO_3$, hexagonal-$PbSiO_3$ and alamosite. Alamosite is the only stable crystalline polymorph, L-$PbSiO_3$ and hexagonal-$PbSiO_3$ are metastable. The crystal structure of alamosite reported by Boucher and Peacor (17) indicates that the unit cell contains parallel metasilicate chains. There are 12 tetrahedra per repeat unit and the chains are strongly buckled. Divalent Pb in alamosite is in pyramidal co-ordination, one triangular and two square pyramids are linked to form spiral chains parallel to (010). It has been suggested on the basis of the close resemblance of the Raman spectra of $PbO.SiO_2$ glass, L-$PbSiO_3$ and alamosite that the metasilicate glass contains disordered chains (11).

Raman spectra of glasses of the $2xCuO.(1-x)PbO.(1-x)SiO_2$ Series containing 0,1,2,4 and 10 mole % of CuO are shown in Fig. 1. The main features for these green coloured glasses are a broad band centred at about 960 cm^{-1}, which has been attributed to Si-O stretching vibrations of disordered $(SiO_3)_n$ groups (11,12); a broad shoulder at about 470 cm^{-1}, indicative of an O-Si-O bending mode (20) and a weak band at about 765 cm^{-1}, which was not assigned. It appears that the Raman spectra fail to show significant alterations (if any) in the glass structure due to CuO doping up to 2 mole %. However, the maximum of the 960 cm^{-1} band has shifted downward to 933 cm^{-1} for the $PbO.SiO_2$ glass containing 10 mole % CuO. Also, the band maximum for the composition containing 4 mole % CuO is split with the lower maximum at 939 cm^{-1}.

Increasing the CuO content of the glass can be expected to have the same effect on the metasilicate framework as an increase in the content of other glass modifiers, including lead, namely a depolymerization of the metasilicate chains to more disconnected silicates. It can be expected that this depolymerization process will lower the maximum of the 960 cm^{-1} band as was observed for $PbO-SiO_2$ glasses when the $PbO:SiO_2$ ratio is increased beyond 1 (11).

An important point to note is the de-enhancement of the host Raman signal as the CuO concentration increases, i.e. as the doped glass becomes darker. On the other hand, for up to 10 mole % of doping no (resonance) Raman signal was observed from the dopant, CuO. This observation is consistent with the picture that the amount of excitation energy absorbed by Cu^{2+} is predominantly dissipated into heat by rapid relaxation through the lower lying excited electronic states (18), which arise from lowering of the octahedral crystal field symmetry and from the spin-orbit interaction (19).

Fig. 2 shows FTIR specular reflectance spectra of the glasses of this series. Two distinct maxima are observed at about 950 cm^{-1} and at about 890 cm^{-1}. There is an increase in the relative intensity of the maximum of the 890 cm^{-1} over that of the 950 cm^{-1} peak with increasing CuO concentration of the glass although the effect is barely noticeable for 1 and 2 mole % CuO. The occurrence of the two maxima at these approximate peak positions has also been found by other investigators who studied the infrared reflectance spectra of lead silicate glasses (20-22). For example,

Worrell and Henshall (22) noted the gradual disappearance of a band at 1000 cm^{-1} and the emergence of a shoulder at 900 cm^{-1} with increasing lead content of the glass. The 900 cm^{-1} band was also found to shift to lower frequencies with increasing lead content.

It seems likely that the downward shift observed in the Raman spectra of the glasses of this series containing 4 and 10 mole % CuO and the relative increase in the intensity of the 890 cm^{-1} over the 950 cm^{-1} band in the FTIR spectra of these glasses with increasing CuO content are related phenomena that originate in the depolymerization of the metasilicate chains to more disconnected silicates. It can be expected that the addition of CuO will have the effect of increasing the modifier content of the glass which will contribute to this depolymerization process through the formation of additional non-bridging $Si\text{-}O^-$ groups.

(2) <u>$3xCuO.(1-x)PbO.2(1-x)SiO_2$ Glasses</u>

Fig. 3 gives Raman spectra for glasses of the series $3xCuO.(1-x)PbO.2(1-x)SiO_2$. All Raman spectra of these dark green coloured glasses derived from the $PbO.2SiO_2$ system are similar except that of the glass containing the highest concentration of CuO (10 mol %). The Raman spectra of the glasses with up to 4 mol % CuO show the characteristic broad asymmetric band with its maximum at 1006-1009 cm^{-1} and a shoulder at 958-897 cm^{-1}. It has been suggested that the former polarized band is primarily due to silicates which are less polymerized than the $(Si_2O_5)_n$ (disilicate) sheet (11).

The similarity of the Raman spectra of the glasses in this series suggests that up to 4 mol % CuO can be accommodated in the glass matrix without apparent changes to the structure of the host network. The Raman spectrum of the glass containing 10 mol % CuO is significantly different from the Raman spectra of the glasses containing up to 4 mol % CuO. In addition to the broad asymmetric band with the band maximum at 1002 cm^{-1} there appears a relatively narrow band with maximum intensity at 913 cm^{-1}. Virgo et al. assigned a band in the 905-920 cm^{-1} range in the Raman spectra of silicate melts to the symmetric stretching frequency of $Si_2O_7^{6-}$ units (23). The observation of the 913 cm^{-1} band suggests that a substantial number of these units are present in the glass containing 10 mol % CuO.

It is noteworthy that the Raman spectra of glasses with nominal compositions $PbO.1.25SiO_2$ and $PbO.1.5SiO_2$ exhibit a shoulder at 912 cm^{-1} to the dominant polarized symmetric stretching band at about 1010 cm^{-1} (11). It is interesting to reflect on the respective roles of Pb and Cu in silicate glasses at this point. The NMR study of Leventhal and Bray has indicated that most of the lead atoms in the $PbO-SiO_2$ system act as network formers even at low (30 mol %) concentrations of PbO (24). The existence of chain-like PbO units in glassy $PbO.SiO_2$ and $PbO.2SiO_2$ has also been indicated by X-ray studies (25). Thus, only a portion of the lead present in the glasses of this study acts as modifier. The addition of CuO to lead containing silicate glasses results in the formation of Cu^{2+} and Cu^{+} ions (26) both of which act as modifiers only.

The pre-eminence of the 913 cm^{-1} band in the Raman spectrum of the glass with 10 mol % CuO as compared to the shoulder at this position for $PbO.1.25SiO_2$ and $PbO.1.5SiO_2$ suggests that Cu is more effective than Pb in depolymerizing the silicate framework in $PbO-SiO_2$ glasses.

As for the $2xCuO.(1-x)PbO.(1-x)SiO_2$ series there are no features in the Raman spectra indicative of Cu groupings in the glass. De-enhancement of the host Raman signal with increasing CuO concentration was also a characteristic feature of glasses of this series.

Like the Raman spectra, the FTIR spectra of the $3xCuO.(1-x)PbO.(1-x)2SiO_2$ glasses (Fig. 4) are quite different from those of the $xCuO.(1-x)PbO.(1-x)SiO_2$ series. The spectrum of the CuO-free glass shows maximum reflectance at 1050 cm^{-1} and there are shoulders at about 950, 890 and 770 cm^{-1}. The spectrum is very similar to the infrared reflectance spectrum of $PbO.2SiO_2$ reported by Worrell and Henshall (20).

The overall shape of the FTIR spectra changes very little for up to 4 mol % CuO but there is a downward shift in the frequency at the band maximum as the CuO concentration increases. Practically no change is noticeable when 1 mole % CuO is added. With 2 mole % CuO there is a slight shift of the maximum to 1040 cm^{-1}. At 4 mole % CuO, the maximum drops to 1022 cm^{-1} and the relative intensity of the shoulders as compared to the intensity at the band maximum increases. At a concentration of 10 mole % CuO the FTIR spectrum changes substantially. The bands at 1022 cm^{-1} and 770 cm^{-1} observed in the spectrum of the glass containing 2 mole % CuO

disappear, leaving a broad band at 935 cm^{-1}. This FTIR spectrum is very similar to that of $PbO.SiO_2$. Since the composition containing 10 mole % CuO can be approximated by the formula $1/6CuO.1/2PbO.SiO_2$ it could be argued that CuO is three times as effective as PbO in creating non-bridging $Si-O^-$ groups in the silicate network.

The results of the Raman and FTIR spectroscopic measurements point in the same direction. Up to 4 mol % CuO can be incorporated with relatively minor changes into the silicate network of $PbO.2SiO_2$. Adding 10 mol % CuO to $PbO.2SiO_2$ results in a depolymerization to a silicate network which contains a substantial proportion of short (metasilicate and pyrosilicate) type units.

It would be premature to speculate in detail on the role of CuO in the lead release of commercial type glazes on the basis of the systems studied here in isolation. Commercial type lead based ceramic glazes are more complex systems containing B_2O_3, Al_2O_3 and other constituents not addressed in this investigation. Furthermore, the glaze firing process introduces additional parameters not considered in this study. Some of these factors will be the subject of further investigations.

(IV) Conclusions

On the basis of the Raman and FTIR spectra of glasses derived from $PbO.SiO_2$ and $PbO.2SiO_2$ to which various amounts of CuO have been added it is concluded that up to about 2 mole % CuO can be added to the former and about 4 mole % CuO to the latter composition without causing significant changes in the structure of the silicate network.

The addition of 10 mole % CuO causes a definite depolymerization of the metasilicate and higher polymerized chains through the creation of non-bridging $Si-O^-$ groups in the silicate network. It appears that the addition of 10 mole % CuO is more effective than an equivalent amount of PbO in the depolymerization of $PbO.2SiO_2$.

(V) Acknowledgment

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TABLE 1

CuO Containing $PbO-SiO_2$ Glasses and Melting Temperature Ranges

Glass Series	Values of X	Melting Temperature Range
$2xCuO.(1-x)PbO.(1-x)SiO_2$,	0.00, 0.01, 0.02, 0.04, 0.10	900-1050°C
$3xCuO.(1-x)PbO.2(1-x)SiO_2$,	0.00, 0.01, 0.02, 0.04, 0.10	1200-1300°C

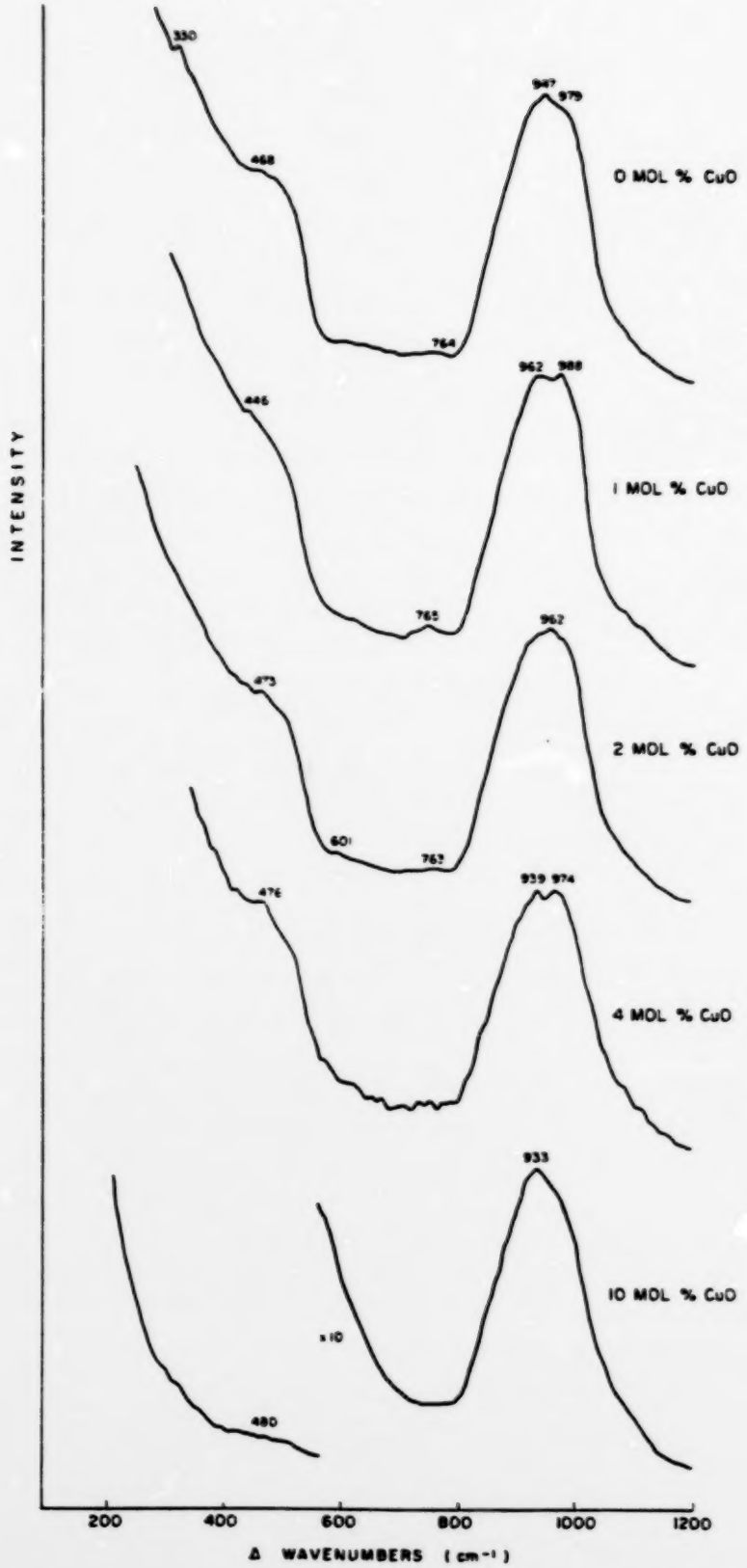

Fig. 1 Raman spectra of glasses of the $2xCuO.(1-x)PbO.(1-x)SiO_2$ series.

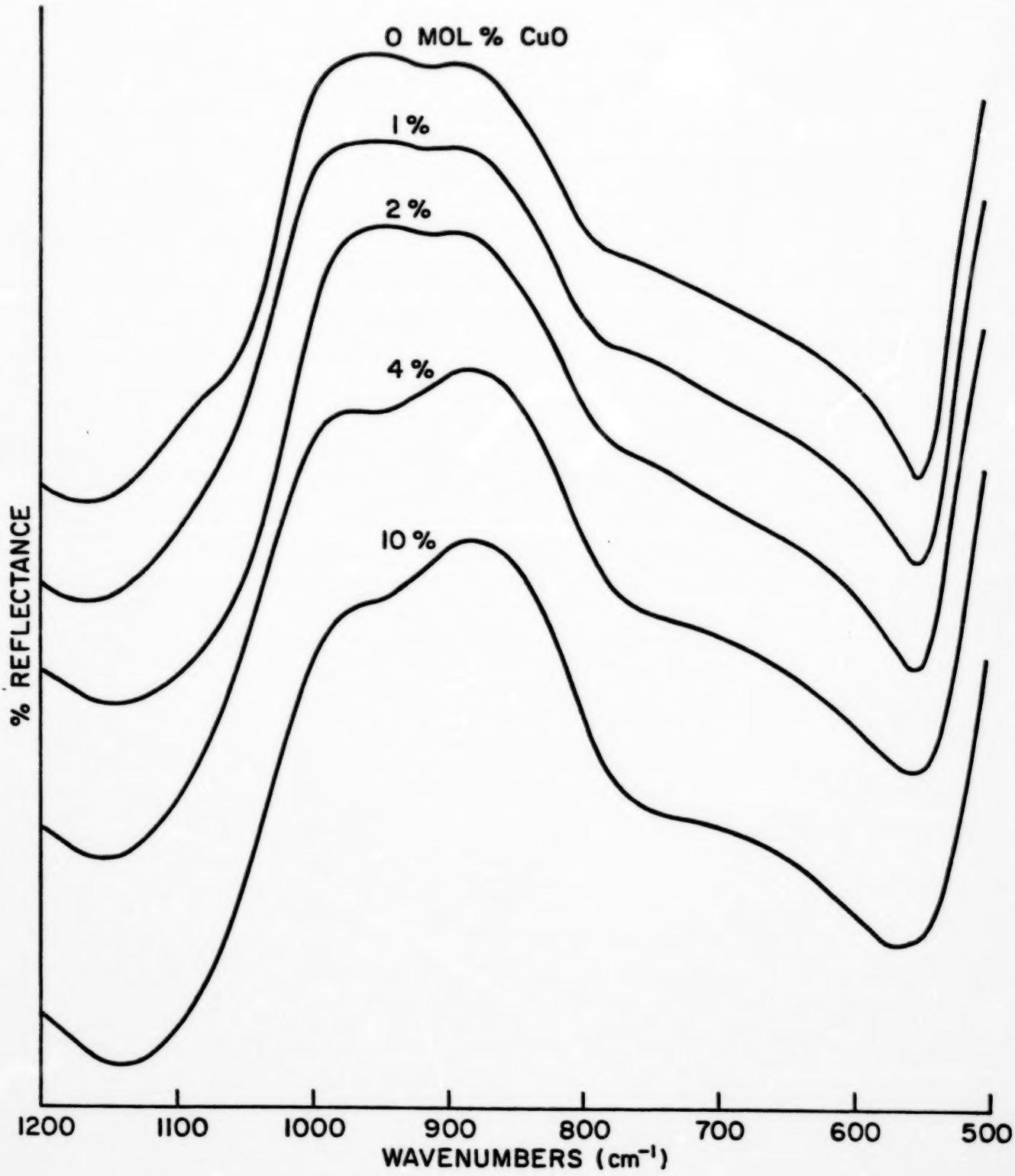

Fig. 2 Fourier Transform Infrared Reflectance spectra of glasses of the $2xCuO.(1-x)PbO.(1-x)SiO_2$ series.

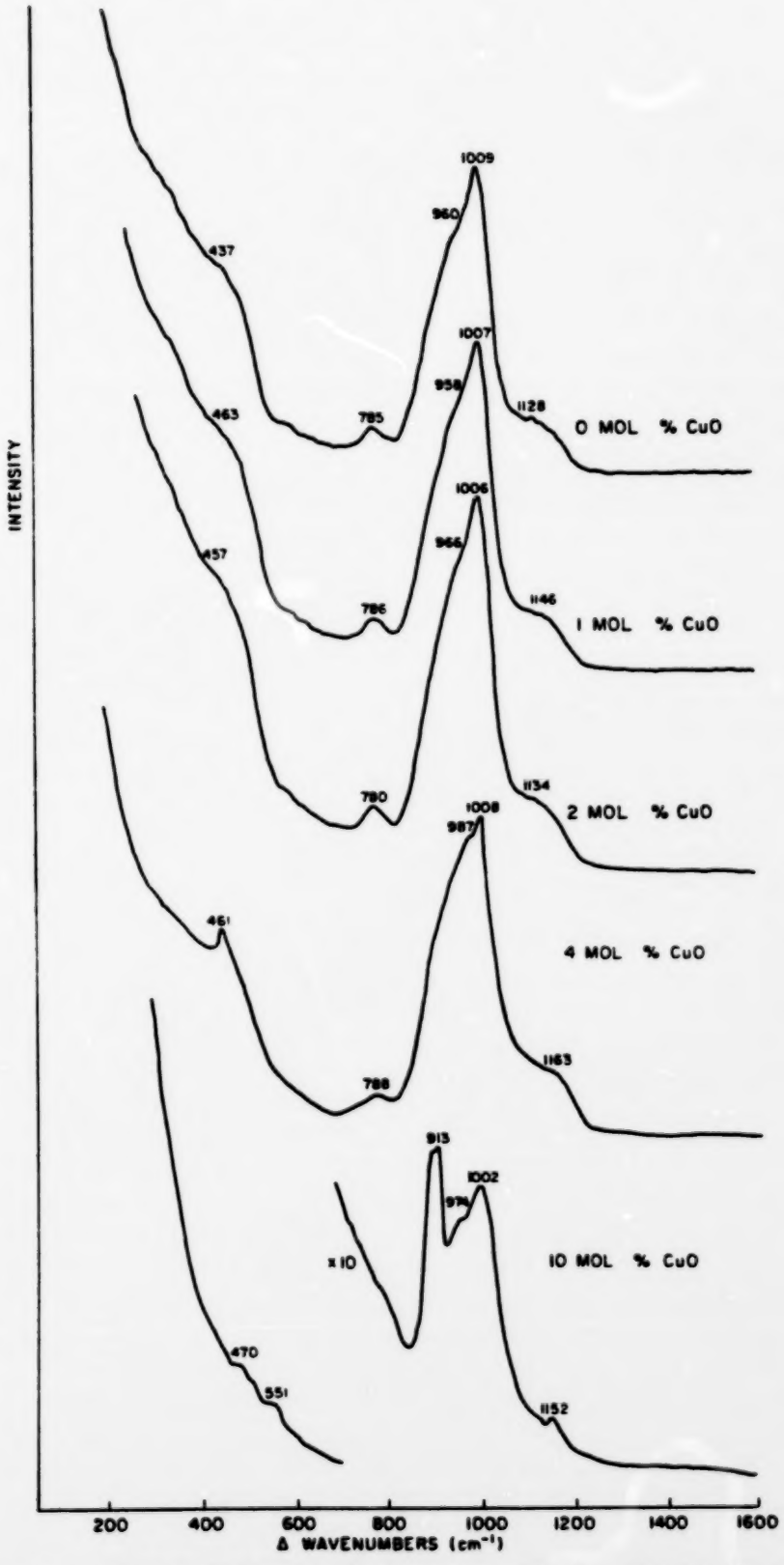

Fig. 3 Raman spectra of glasses of the $3xCuO.(1-x)PbO.2(1-x)SiO_2$ series.

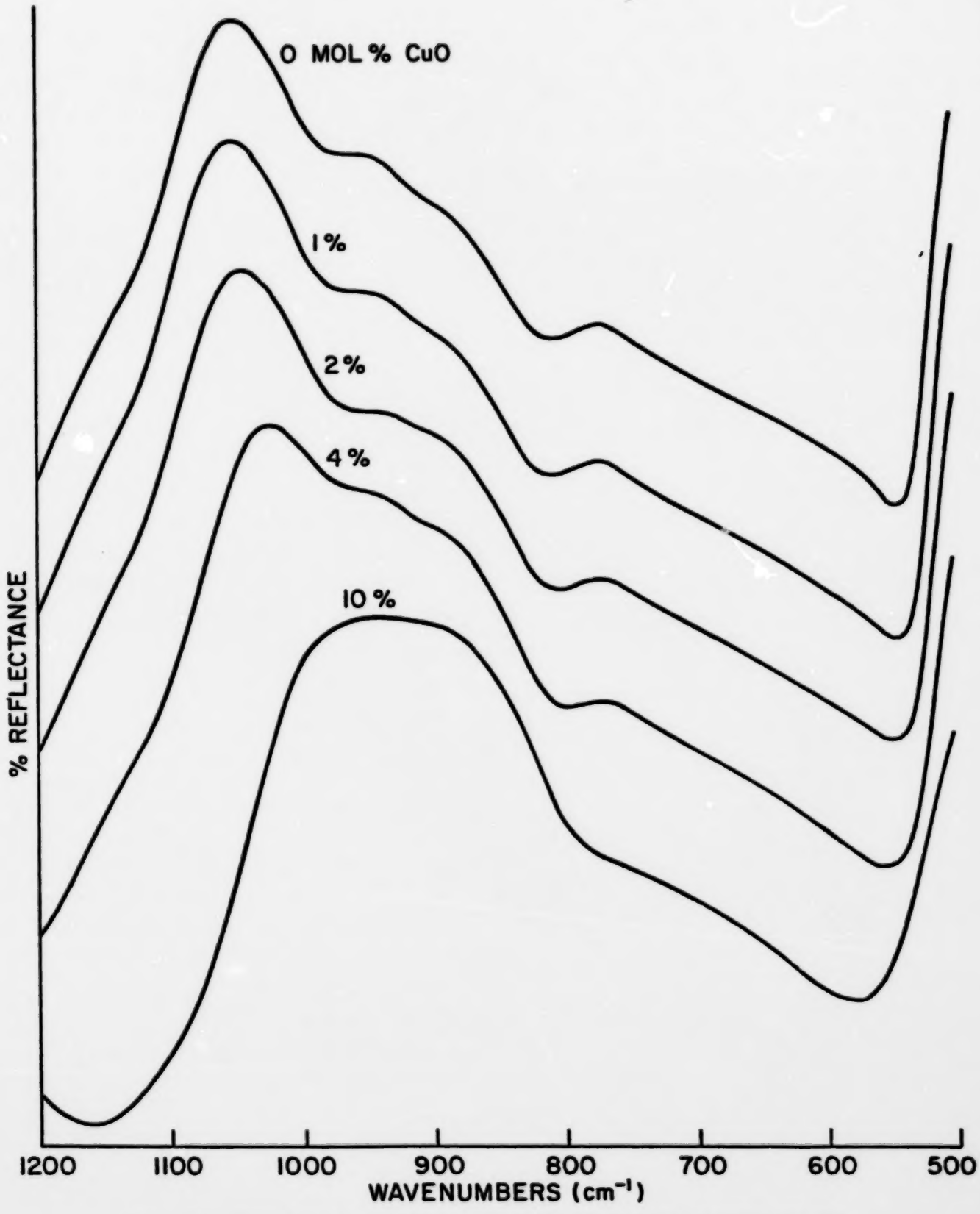

Fig. 4 Fourier Transform Infrared Reflectance spectra of glasses of the $3xCuO.(1-x)Pb0.2(1-x)SiO_2$ series.

Fig. 1 Raman spectra of glasses of the $2xCuO.(1-x)PbO.(1-x)SiO_2$ series.

Fig. 2 Fourier Transform Infrared Reflectance spectra of glasses of the $2xCuO.(1-x)PbO.(1-x)SiO_2$ series.

Fig. 3 Raman spectra of glasses of the $3xCuO.(1-x)PbO.2(1-x)SiO_2$ series.

Fig. 4 Fourier Transform Infrared Reflectance spectra of glasses of the $3xCuO.(1-x)PbO.2(1-x)SiO_2$ series.